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A MODIFIED CELL-CLUSTER THEORY FOR THE SOLID STATE WITH APPLICATION TO THE HARMONIC MODEL

by

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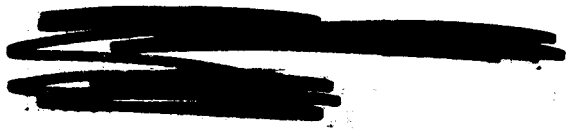
ABSTRACT

A modified cell cluster theory for calculating the specific free energy of a solid is applied to a harmonic model of a perfect monatomic crystal corresponding to the two dimensional triangular lattice with nearest neighbor interactions only. This technique starts with the single particle (Einstein) theory and then evaluates corrections from correlated motion of larger and larger sets of contiguous particles. In the high temperature limit the general harmonic theory leads to an expression for the Helmholtz free energy, F_N, in the form,

$$F_N/NkT = -2 \ln T^* + D_N$$

with $T^* = kT/h\nu_0$. For the Einstein model $D_N = 1.0986 \cdots$ while the modified cell cluster technique carried through sixth order gives $D_N = 0.8565 \cdots$. The technique is also applied to a one dimensional harmonic model. From these and earlier studies we are led to the conclusion that a cell cluster theory is an appropriate method for treating anharmonic forces in a solid particularly at high temperatures and pressures.



I. INTRODUCTION

With the advent of new experimental results on the high temperature, high pressure properties of solids there has in the last five years been a renewed interest in the theory of the anharmonic properties of solids. Most of the work[1] has started with the classical harmonic approximation and has treated anharmonic effects by perturbation theory. This approach, while extremely important theoretically, would not be appropriate at very high temperatures where anharmonic forces may play a dominant role in the thermodynamic and elastic properties.

In a recent paper[2] a technique was developed for estimating the free energy of the most extreme anharmonic model, a system of rigid spheres, at very high compressions. Although the original aim of the work in Ref. (2) was to obtain only the limiting value of the Helmholtz free energy per particle as $V/V_0 \to 1$ (V_0 is the close-packed value of the volume V), one might very well consider this technique for treating anharmonic forces in general. The method starts from the single particle or Einstein approximation and then evaluates the specific free-energy contributions from correlated motion of larger and larger sets of contiguous particles. This type of sequential approximation has also been considered by Runnels[3] who applied it to a one-dimensional system of hard lines.

The major purpose of the present paper is to apply this technique to a purely harmonic model of a simple crystal and to examine the method for this simplified case. Since the earlier calculations[2] were performed for a system of two dimensional rigid discs in a close-packed hexagonal structure we choose as our model a two dimensional triangular lattice with only nearest neighbor interactions. In this manner we obtain results for the same geometric lattice at the two extremes, the harmonic approximation and the rigid disc system.

There arises naturally the question about the convergence of our sequence of approximations. While we have been unable to prove anything in general (other than that the entire sequence carried out to N'th order is an identity for the exact free energy of N particles) the procedure has been carried out through 4th order (all

correlations of four particles) for rigid discs[2] and in this paper through sixth order (all correlations of six particles) for the harmonic model. Both results give every appearance of generating a convergent sequence of approximations.

The technique we employ is closely related to the cell-cluster theory[4] developed by J. De Boer and his coworkers. However it is a modification which avoids the difficult combinatorial problems that have been associated with the cell cluster theory.

Although our primary purpose is to investigate a theory that would be suitable for highly anharmonic solids one might also ask whether this technique can be used for calculating the thermodynamic properties of an ideal crystal in the harmonic approximation. Since we consider only corrections to the Einstein approximation due to the correlated motion of small groups of contiguous particles one realizes that this is intrinsically a high temperature approximation and cannot represent the long wavelength part of the lattice frequency distribution function. Moreover, a general development of the high temperature crystalline entropy in the harmonic approximation can be expressed in terms of a well defined perturbation series about the Einstein model and this development has been carried out by Salter.[5] Salter's series is based upon the complete dynamical matrix for the lattice and as such is a more suitable and more elegant way of treating the purely harmonic approximation. However it cannot be so readily modified to treat large anharmonic effects.

II. BASIC METHOD

Although the approximation scheme described below can in principle be applied to three dimensional, multi-component crystals including certain types of defects, for the sake of illustration we consider a perfect monatomic crystal corresponding to the two dimensional triangular lattice shown in Fig. 1. Moreover we restrict ourselves to nearest neighbor interactions.

We are interested in a series of free energy functions for subfigures of the lattice. A subfigure is a set of ℓ arbitrarily chosen lattice sites with all possible nearest neighbor bonds drawn among the ℓ sites. From all possible subfigures we will consider

only connected ones (see table I for examples).

To define the free energy function for a connected subfigure we fix all atoms at their lattice sites except for the ℓ atoms in the subfigure and analyze the harmonic vibrations of these ℓ atoms. (See appendix A for an outline of this analysis.) From these results we can evaluate the partition function for the atomic vibrations, which in two dimensions has the form

$$Q_{\ell,t} = \prod_{\alpha=1}^{2\ell} \exp\left(-1/2\beta h\nu_{\alpha,\ell,t}\right)/\left[1-\exp(-\beta h\nu_{\alpha,\ell,t})\right] \qquad \text{(II -1)}$$

$$\beta = 1/kT$$

The $\nu_{\alpha,\ell,t}(\alpha = 1,2\cdots, 2\ell)$ are the frequencies of the 2ℓ normal modes of the connected subfigure with ℓ atoms of configuration t. The constants k and h are Boltzmann's constant and Planck's constant respectively and T is the absolute temperature. Note that we use two indices to identify each figure. The first, ℓ, gives the number of atoms in the figure, and the second, t, identifies the configuration.

The figures are numbered in the arbitrary manner given in table I. For each subfigure we can then calculate a vibrational Helmholtz free energy function, F, by

$$F_{\ell,t} = -kT \ln Q_{\ell,t} \qquad \text{(II-2)}$$

To describe a macroscopic crystal we need to obtain the free energy F_N for an N atom system with $N \cong 10^{23}$. To calculate F_N we propose to adopt a systematic series of approximations based on the functions $F_{\ell,t}$ for small ℓ. First we define a series of functions $W_{\ell,t}$ by means of recursion formulas as illustrated below for the first few cases. See table I for figure references.

$$\begin{aligned}
F_{1,1} &= W_{1,1} \\
F_{2,1} &= 2W_{1,1} + W_{2,1} \\
F_{3,1} &= 3W_{1,1} + 2W_{2,1} + W_{3,1} \\
F_{3,2} &= 3W_{1,1} + 2W_{2,1} + W_{3,2} \\
F_{3,3} &= 3W_{1,1} + 3W_{2,1} + W_{3,3}
\end{aligned} \qquad \text{(II-3)}$$

The function $W_{1,1}$ is a single particle free energy and we obtain the Einstein approximation to F_N by the relation

$$F_N = NW_{1,1} \tag{II-4}$$

The two particle free energy $F_{2,1}$ is equated to this Einstein approximation plus a correction term $W_{2,1}$. The $W_{2,1}$ can be considered to be the free energy for a pair analogous to the pair potential function in the potential energy of a system. For each figure we first approximate $F_{\ell,t}$ by the Einstein approximation $\ell W_{1,1}$ and then correct this for all pairs, triplets, and so on, up to the ℓ - 1 particle subfigures contained in the figure under consideration. In each case the correction factor is given by some constant times the appropriate W. The difference between the exact $F_{\ell,t}$ and this series of approximations then defines a new $W_{\ell,t}$.

In general

$$F_{\ell,t} = \sum_{i=1}^{\ell-1} \sum_{j=1}^{T_i} C_{i,j}^{\ell,t} W_{i,j} + W_{\ell,t} \tag{II-5}$$

where T_i is the number of different configurations of a connected subfigure of i particles (see table I) and the $C_{i,j}^{\ell,t}$ are the number of figures of type (i,j) contained in the figure (ℓ,t).

If we now extend this relation to a macroscopic crystal of N particles and ignore boundary effects (e.g. one can consider a square crystal with periodic boundary conditions) we obtain

$$\begin{aligned} F_N &= NW_{1,1} + 3NW_{2,1} + 3NW_{3,2} + 6NW_{3,2} + 2NW_{3,3} + \cdots \\ &= N \sum_{\ell=1}^{N} \sum_{t=1}^{T_\ell} g_{\ell,t} W_{\ell,t} \end{aligned} \tag{II-6}$$

where $Ng_{\ell,t}$ is the number of ways in which the (ℓ,t) figure can be placed on the lattice. The combinatorial analysis for obtaining the $g_{\ell,t}$ is given in appendix B and the $g_{\ell,t}$ for ℓ = 1,2,3,4,5,6 are given in table I. Physically we can think of first approximating the N particle crystal by N equivalent and independent oscillators and then

successively correcting for all two, three, four and higher order particle correlations. Although we can prove nothing about the convergence of this series of approximations, one hopefully needs only terms for small ℓ to obtain sufficiently accurate values for F_N.

Since this scheme ignores long wavelength, i.e. low frequency, modes it appears that it will be valid only at high temperatures. Therefore we concentrate our attention on the high temperature limiting form of $Q_{\ell,t}$:

$$Q_{\ell,t} = \prod_{\alpha=1}^{2\ell} kT/h\nu_{\alpha,\ell,t} \qquad \text{(II-7)}$$

Since we consider only nearest neighbor interactions with a simple force constant all frequencies $\nu_{\alpha,\ell,t}$ are proportional to a fundamental frequency ν_o:

$$\nu_{\alpha,\ell,t} = b_{\alpha,\ell,t}\,\nu_o$$
$$\nu_o = \frac{1}{2\pi}\left(\frac{\varkappa}{m}\right)^{1/2} \qquad \text{(II-8)}$$

where $\varkappa$ is the force constant for nearest neighbor interactions and m is the mass of one atom. In this treatment we regard ν_o as a parameter and express all our results in terms of a reduced temperature T*.

$$T^* = T/\theta \qquad \text{(II-9)}$$
$$\theta = h\nu_o/\varkappa$$

Thus equation (II-7) can be expressed in the form

$$Q_{\ell,t} = \left(\frac{T}{\theta}\right)^{2\ell} \prod_{\alpha=1}^{2\ell} (1/b_{\alpha,\ell,t}) \qquad \text{(II-10)}$$

and

$$\frac{F_{\ell,t}}{kT} = -2\ell \ln T^* + D_{\ell,t} \qquad \text{(II-11)}$$

with

$$D_{\ell,t} = \sum_{\alpha=1}^{2\ell} \ln b_{\alpha,\ell,t}.$$

Moreover since the $W_{\ell,t}/kT$ with $\ell > 1$ are independent of T* and can be computed from the $D_{\ell,t}$ terms, we obtain for a macroscopic N particle system the following form for the free

energy.

$$F_N/kT = -2N \ln T^* + ND_N \qquad \text{(II-12)}$$

where D_N can be computed from the series

$$D_N = D_{1,1} + (1/kT) \sum_{\ell=1}^{N} \sum_{t=1}^{N_\ell} g_{\ell,t} W_{\ell,t} \qquad \text{(II-13)}$$

and the modified recursion relations, which follow from equations (II-3) and (II-11) are

$$D_{2,1} = 2D_{1,1} + W_{2,1}/kT$$

$$D_{3,1} = 3D_{1,1} + 2W_{2,1}/kT + W_{3,1}/kT \qquad \text{(II-14)}$$

Thus we can, in the high temperature limit, focus our attention on the constant D_N and ask how well it is approximated by a few terms in the series of equation (II-13).

III. RESULTS FOR THE TRIANGULAR LATTICE

In the single particle Einstein Model one obtains for the high temperature limit of the free energy per particle

$$F_N/NkT = -2 \ln T^* + 1.0986. \qquad \text{(III-1)}$$

Collecting all the terms in the series in Eq. (II-13) for each value of ℓ we have for successive terms in the expansion of the free energy per particle

$$F_N/NkT = -2 \ln T^* + \sum_{\ell=1}^{N} d_\ell , \qquad \text{(III-2)}$$

$$d_\ell = \sum_{t=1}^{T_\ell} g_{\ell,t} \tilde{D}_{\ell,t} \quad : \quad \tilde{D}_{\ell,t} = W_{\ell,t}/kT$$

The high temperature corrections, $\tilde{D}_{\ell,t}$, due to each figure are given in table I. The sum of all terms for each order ℓ through sixth order yields the following results.

$$\begin{aligned} d_1 &= 1.0986 & d_4 &= -0.0129 \\ d_2 &= -0.1767 & d_5 &= -0.0106 \\ d_3 &= -0.0342 & d_6 &= -0.0077 \end{aligned} \qquad \text{(III-3)}$$

This gives an estimate of the free energy per particle through sixth order of

$$F_N/NkT \tilde{=} -2 \ln T^* + 0.8565 \qquad \text{(III-4)}$$

In Fig. 2 the successive estimates for the constant D_N are plotted as a function of

$1/\sqrt{\ell}$. Extrapolating graphically to $\ell = \infty$ we can also obtain as an extrapolated estimate for the free energy per particle

$$F_N/NkT \cong -2 \ln T^* + 0.79 \qquad \text{(III-5)}$$

The successive corrections to the Einstein model through sixth order have also been carried out for the complete free energy function given by Eqs. (II-1) and (II-2). These results are displayed in Fig. (3) where the difference, $\Delta F_N/NkT$, between the given order of approximation and the Einstein model is plotted as a function of $1/\sqrt{\ell}$ for five isotherms.

$$\Delta F_N = F_N(\text{Einstein}) - F_N(\text{order } \ell) \qquad \text{(III-6)}$$

There is a suprisingly small temperature dependence in the rate of convergence of this series of approximations.

While the results for rigid disks[2] through fourth order gave only a very small correction (approximately .1% in the free energy per particle) to the single particle or cell theory, we find that the same technique applied to the harmonic oscillator model gives a relatively large correction to the single particle theory. The series of corrections appears to converge although rather slowly. Empirically we find that the successive corrections decrease linearly with $1/\sqrt{\ell}$ where ℓ is the number of particles in the cluster.

The calculation given here leads us to conclude that a modified cell-cluster technique is an appropriate way to generate successive approximations to the free energy function. We hope to extend these calculations to anharmonic models in the future.

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APPENDIX A: HARMONIC ANALYSIS OF CELL CLUSTERS ON A TRIANGULAR LATTICE

Restricting ourselves to nearest neighbor interactions we can regard each cell cluster as a collection of point masses and elastic springs. The set of springs under consideration are those associated with the bonds of each figure in Table I plus the interactions between the vibrating particles and the neighboring fixed particles. Fig. 4 illustrates this for a typical six particle cluster (6, 24 from Table I). The 12 coordinates (an x,y coordinate for each particle) which describe this system are also given in Fig. 4.

The potential energy for such a system can be written as a sum over all bonds or "springs" (29 terms in the case of cluster 6,24) with a single force constant, κ.

$$V = \frac{1}{2}\kappa \sum_{\alpha} (\Delta R_\alpha)^2 \qquad \text{(A-1)}$$

$$\Delta R_\alpha = \left| \underset{\sim}{R}_{0\alpha} + \underset{\sim}{r}_{2\alpha} - \underset{\sim}{r}_{1\alpha} - \underset{\sim}{R}_{0\alpha} \right|$$

$\underset{\sim}{R}_{0\alpha}$ = vector between the lattice sites associated with bond α

The displacement vectors for the two particles associated with bond α are denoted by $\underset{\sim}{r}_{1\alpha}$ and $\underset{\sim}{r}_{2\alpha}$. In the case of a bond between one of the vibrating particles and a fixed particle $\underset{\sim}{r}_{2\alpha}$ is identically zero.

Each $(\Delta R_\alpha)^2$ can be expanded in terms of the displacement vectors to give in diadic form

$$V = \sum_{\alpha} \Big\{ \underset{\sim}{r}_{1\alpha} \cdot \frac{\underset{\sim}{R}_{0\alpha}\underset{\sim}{R}_{0\alpha}}{R_{0\alpha}^2} \cdot \underset{\sim}{r}_{1\alpha} + \underset{\sim}{r}_{2\alpha} \cdot \frac{\underset{\sim}{R}_{0\alpha}\underset{\sim}{R}_{0\alpha}}{R_{0\alpha}^2} \cdot \underset{\sim}{r}_{2\alpha} - \underset{\sim}{r}_{1\alpha} \cdot \frac{\underset{\sim}{R}_{0\alpha}\underset{\sim}{R}_{0\alpha}}{R_{0\alpha}^2} \cdot \underset{\sim}{r}_{2\alpha} \Big\} \qquad \text{(A-2)}$$

Thus each bond contributes three 2 x 2 blocks to the 12 x 12 dynamic matrix. The contribution being specified by the dyad $\underset{\sim}{R}_{0\alpha}\underset{\sim}{R}_{0\alpha}/R_{0\alpha}^2$, where $R_{0\alpha}$ is the magnitude of the vector $\underset{\sim}{R}_{0\alpha}$. In the triangular lattice there are three different cases. Letting $\underset{\sim}{i}$ and $\underset{\sim}{j}$ be the unit vectors along the x and y cartesian coordinates respectively and a denote the lattice distance we have

Case 1: $$\underset{\sim}{R}_0 = \frac{a}{2}\,\underset{\sim}{i} + \frac{3a}{2}\,\underset{\sim}{j} \;:\; \frac{\underset{\sim}{R}_0\underset{\sim}{R}_0}{R_0^2} = \begin{pmatrix} \frac{1}{4} & \frac{3}{4} \\ \frac{3}{4} & \frac{3}{4} \end{pmatrix} \qquad \text{(A-3)}$$

Case 2: $$\underset{\sim}{R}_0 = a\,\underset{\sim}{i} \;:\; \frac{\underset{\sim}{R}_0\underset{\sim}{R}_0}{R_0^2} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \qquad \text{(A-4)}$$

Case 3: $$\underset{\sim}{R}_0 = \frac{1}{2}\,a\,\underset{\sim}{i} - \frac{3}{2}\,a\,\underset{\sim}{j} \;:\; \frac{\underset{\sim}{R}_0\underset{\sim}{R}_0}{R_0^2} = \begin{pmatrix} \frac{1}{4} & -\frac{3}{4} \\ -\frac{3}{4} & \frac{3}{4} \end{pmatrix}$$

In actual practice the dynamical matrix for each figure was set up automatically by a computer in an orthogonal cartesian coordinate system. The computer accepted as input a description of each figure then automatically cycled through the set of bonds, identified each with one of the above three cases and added the appropriate numbers to the appropriate elements of the dynamical matrix. After forming each matrix the eigenvalues were obtained numerically by the general computer program which then proceeded to calculate the partition function and free energy for that figure.

APPENDIX B: COMBINATORIAL PROBLEMS †

In the formulation of successive corrections to the Einstein model we encounter two combinatorial problems. The first one involves obtaining the number $C_{i,j}^{\ell,t}$ of Eq. (II-5), namely the number of ways a figure of type (i,j) can be contained or placed on a figure of type (ℓ,t) where $\ell > t$. This count was obtained by simple brute force counting for each figure. The first few results can be found in Eq. (II-3). However, a table containing the results for all figures through six particles would be prohibitative in length and we hope that the following few additional examples will adequately explain the concept. The reader is referred to Table I for the code notation of each figure

$$F_{5,8} = 5W_{1,1} + 5W_{2,1} + 2W_{3,1} + 2W_{3,2} + W_{3,3} + W_{4,2} + 2W_{4,3} + W_{5,8} \qquad \text{(B-1)}$$

$$F_{6,37} = 6W_{1,1} + 8W_{2,1} + 2W_{3,1} + 4W_{3,2} + 3W_{3,3} + 2W_{4,2} + 4W_{4,3} + W_{4,4} + 2W_{4,7} + 2W_{5,6} + 2W_{5,9} + W_{5,14} + W_{6,37}$$

The second problem arises in counting the number of times that a given figure can be placed on a large lattice of N sites or, in other words, the number of different ways the given correlated motion can occur among the N particles of a large lattice. In this problem we consider a system under periodic boundary conditions or ignore any effect due to the boundaries of the system. The general solution to this problem can be given in terms of the symmetry of each figure.

In a general figure pick one point arbitrarily and identify it as the "origin" for this figure. This "origin" can then be placed at any of N lattice positions. For each position of the "origin" we can rotate the figure about this "origin" point through successive angles of 60° and obtain six equivalent figures.

Next consider the mirror image of the given figure obtained by reflection through a line in the plane. Again place the "origin" point on any one of the N lattice sites and by repeated rotation generate again 6N equivalent figures. Thus we see that the maximum number of ways a given figure can be placed on a lattice is 12N.

We now ask, in counting these 12N positions of the figure, how many figures have been counted more than once? (a) If the figure has line of symmetry, its mirror image is equivalent to one of the rotated structures and we have counted every figure twice. (b) If the figure has an n-fold rotational axis of symmetry perpendicular to the plane we will count each figure n times in the process described above. Thus in general we find that

$$Ng_{\ell,t} = 12N/P_{\ell,t}n_{\ell,t} \qquad \text{(B-2)}$$

$$P_{\ell,t} = \begin{cases} 2 & \text{if the figure has a line of symmetry} \\ 1 & \text{otherwise} \end{cases}$$

$n_{\ell,t}$ = order of a perpendicular rotational axis of symmetry

In this manner the combinatorial numbers $g_{\ell,t}$, given in table I were obtained.

APPENDIX C: MONATOMIC ONE-DIMENSIONAL CRYSTAL

The method of successive approximations to the Helmholtz Free Energy as outlined in section II can be easily carried to high order for the one-dimensional crystal. In the first place the recursion relations given by Eq. (II-3) for the triangular lattice take the following simple form

$$F_\ell = \sum_{s=1}^{\ell} (\ell - s + 1)\, W_s \tag{C-1}$$

for the one-dimensional case. This then implies that

$$\begin{aligned} W_1 &= F_1 \\ W_2 &= F_2 - 2F_1 \\ W_\ell &= F_\ell - 2F_{\ell-1} + F_{\ell-2} \qquad \ell > 2 \end{aligned} \tag{C-2}$$

Moreover, since the lattice vibration problem can be solved explicitly[6] in this case each F_ℓ can be calculated from the relation

$$F_\ell/kT = \sum_{s=1}^{\ell} \{\cos \varphi_s/T^* + \ln(1-\exp[-2\cos \varphi_s/T^*])\}$$

$$\varphi_s = s\pi/2(\ell+1) \tag{C-3}$$

The final result in which the free energy of a macroscopic system of N particles is expressed as a series of ℓ particle correlation corrections has the simple form

$$F_N/NkT = \sum_{\ell=1}^{N} W_\ell /kT \tag{C-4}$$

Fig. (5) displays a summary of the one-dimensional results. The exact result for F_N/NkT in the thermodynamic limit was calculated from the known frequency distribution function.[6] Although the rate of convergence of this series appears to be rather slow the ℓth order result is a smoothly varying function of $1/\ell$ becoming linear in $1/\ell$ for large ℓ. It is also interesting to note that the error in truncating the series rapidly becomes independent of temperature for $\ell \cong 6$.

FOOTNOTES

* Parts of this research were carried out by the senior students in the statistical thermodynamics course at the Rice University as a course assignment during the spring semester of 1965. The students contributing to this analysis were D. R. Appelt, F. M. Brasch, J. B. Castillo, R. T. Collier, L. B. Dean, R. M. Evans, M. L. Fontenot, J. W. Hansberry, C. R. Head, D. G. Holland, L. E. Howard, J. W. Howze, A. T. Hunter, C. D. Hyatt, C. B. Jones, C. W. Keilers, K. Y. Maxham, G. A. Mayfield, T. W. Miller, J. A. Musselman, J. T. O'Connell, T. K. Phelps, J. M. Power, S. B. Smith, J. A. Sprague, P. A. Torgrimson, C. R. Underwood, Jr., W. C. Voigt, D. M. Gilliam, J. V. Clifton, A. K. Schwartz, Jr., J. T. F. Kao, A. T. Hu, J. E. Park, R. T. Beaubouef, L. D. Russell, R. C. Clarke, C. M. McBride, R. W. Kennemer, W. M. Salathiel, E. Sorenson, P. S. Davis and L. N. January.

† Mr. Richard W. Kennemer, one of the undergraduate students mentioned before, contributed the analysis of this section.

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TABLE I

Catalog of the various configurations of the connected subfigures with six or fewer particles, including the identification (ℓ,t) and the associated combinatorial factor $g_{\ell,t}$. $\tilde{D}_{\ell,t}$ are the high temperature corrections to the Helmholtz free energy per particle for the figure (ℓ,t). c(-e) denotes c x 10^{-e}.

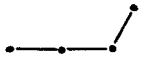
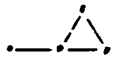
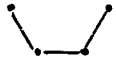
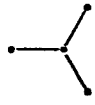
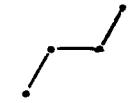
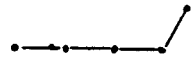
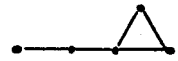
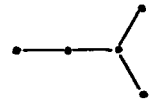
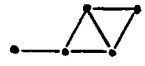
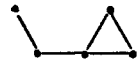
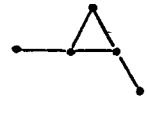
Figure	$\tilde{D}_{\ell,t}$	ℓ,t	$g_{\ell,t}$
	-5.889152(-2)	2,1	3
	-7.874179(-3)	3,1	3
	-1.956950(-3)	3,2	6
	+5.642560(-4)	3,3	2
	-1.135074(-3)	4,1	3
	-2.801903(-4)	4,2	12
	+1.314161(-5)	4,3	12
	-2.544334(-3)	4,4	3
	-6.920867(-5)	4,5	6
	+2.238464(-4)	4,6	2
	-6.920838(-5)	4,7	6
	-1.653166(-4)	5,1	3
	-4.165967(-5)	5,2	12
	-3.130337(-6)	5,3	12
	-2.589990(-5)	5,4	6
	+3.100016(-5)	5,5	6
	-3.677286(-4)	5,6	12
	-6.102255(-7)	5,7	12
	+2.335039(-5)	5,8	12

TABLE I (continued)

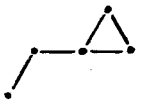
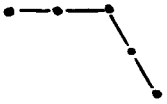
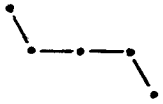
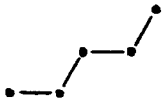
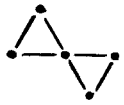
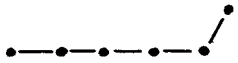
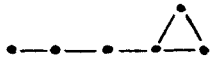
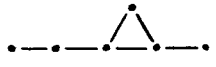
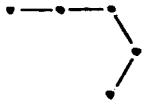
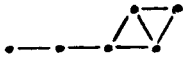
Figure	$\widetilde{D}_{\ell,t}$	ℓ,t	$g_{\ell,t}$	Figure	$\widetilde{D}_{\ell,t}$	ℓ,t	$g_{\ell,t}$
	-6.651535(-7)	5,9	12		-4.021960(-5)	5,19	6
	-1.012356(-5)	5,10	6		-1.005453(-5)	5,20	6
	-9.932433(-6)	5,11	12		+7.681256(-6)	5,21	12
	-8.276314(-4)	5,12	6		-2.453402(-6)	5,22	6
	-7.368526(-6)	5,13	6		-2.411324(-5)	6,1	3
	-6.516965(-5)	5,14	3		-5.054037(-6)	6,2	12
	+5.315820(-5)	5,15	6		+3.212535(-7)	6,3	12
	-2.453107(-6)	5,16	12		-4.578174(-6)	6,4	12
	-9.932031(-6)	5,17	12		-5.331002(-5)	6,5	12
	-2.453749(-6)	5,18	6		-2.308170(-7)	6,6	12

TABLE I (continued)

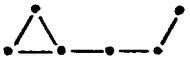
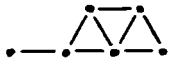
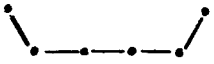
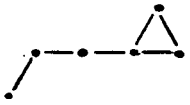
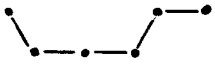
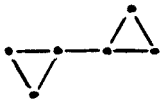
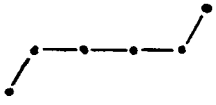
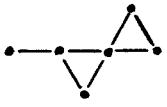
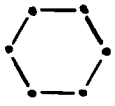
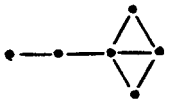
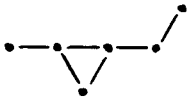
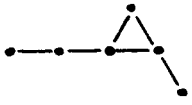
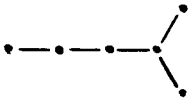
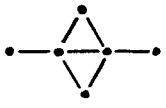
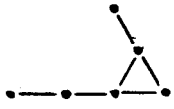
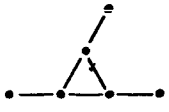
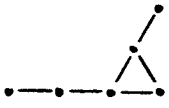
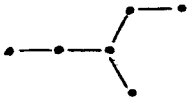
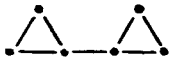
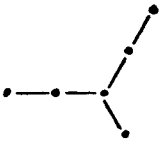
Figure	$\hat{D}_{\ell,t}$	ℓ,t	$g_{\ell,t}$	Figure	$\tilde{D}_{\ell,t}$	ℓ,t	$g_{\ell,t}$
	+7.265171(-7)	6,7	12		-1.459936(-4)	6,17	12
	+3.184141(-7)	6,8	6		+7.769941(-7)	6,18	12
	-3.561017(-7)	6,9	12		-5.447873(-8)	6,19	6
	+3.184177(-7)	6,10	6		-9.303007(-6)	6,20	12
	-4.505846(-5)	6,11	1		-5.953661(-7)	6,21	6
	-1.761855(-7)	6,12	12		+1.730139(-5)	6,22	12
	+6.272596(-6)	6,13	6		-1.227880(-5)	6,23	3
	+7.544033(-6)	6,14	12		+5.672549(-6)	6,24	12
	+2.719698(-6)	6,15	12		+8.886209(-6)	6,25	25
	-1.640565(-7)	6,16	6		+4.310650(-6)	6,26	6

TABLE I (continued)

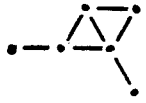
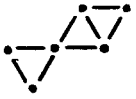
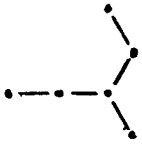
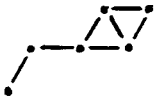
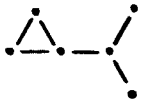
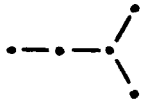
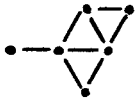
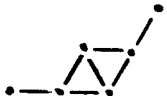
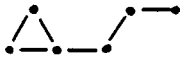
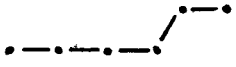
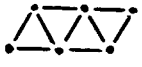
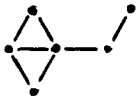
Figure	$\tilde{D}_{\ell,t}$	ℓ,t	$g_{\ell,t}$	Figure	$\tilde{D}_{\ell,t}$	ℓ,t	$g_{\ell,t}$
	+2.919373(-5)	6,27	12		-4.538573(-6)	6,37	6
	+1.204535(-6)	6,28	12		-1.327272(-5)	6,38	12
	+1.970948(-7)	6,29	12		-1.488188(-7)	6,39	12
	+2.320054(-6)	6,30	12		+2.714931(-5)	6,40	12
	-5.222400(-5)	6,31	6		-7.590461(-8)	6,41	12
	-4.876445(-5)	6,32	6		-7.643939(-8)	6,42	12
	-7.865284(-5)	6,33	12		+1.840956(-6)	6,43	12
	-7.675683(-5)	6,34	12		+2.658253(-7)	6,44	6
	-1.339669(-5)	6,35	12		-5.531856(-7)	6,45	12
	-4.497678(-4)	6,36	6		-1.670396(-7)	6,46	12

TABLE I (continued)

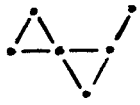
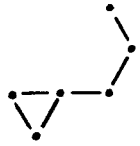
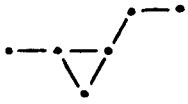
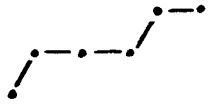
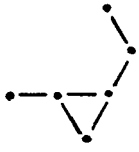
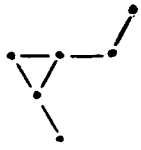
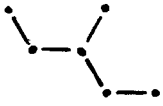
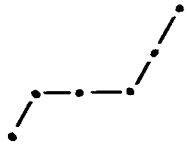
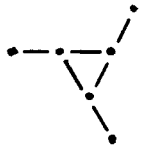
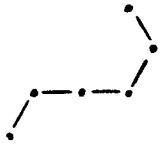
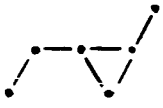
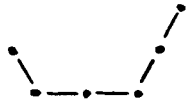
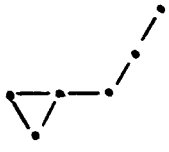
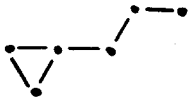
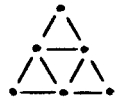
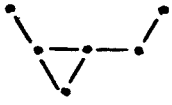
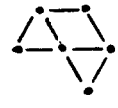
Figure	$\tilde{D}_{\ell,t}$	ℓ,t	$g_{\ell,t}$	Figure	$\tilde{D}_{\ell,t}$	ℓ,t	$g_{\ell,t}$
	-3.651692(-6)	6,47	12		-1.267472(-8)	6,56	12
	+6.484479(-7)	6,48	12		-2.869692(-7)	6,57	12
	+5.933998(-7)	6,49	12		+1.889715(-6)	6,58	12
	+2.651359(-7)	6,50	6		-1.374725(-6)	6,59	12
	+1.117337(-5)	6,51	4		-2.870238(-7)	6,60	12
	+7.848666(-7)	6,52	12		-1.442886(-6)	6,61	12
	-9.763426(-8)	6,53	12		-3.551613(-7)	6,62	12
	-2.151137(-8)	6,54	12		-7.466792(-5)	6,63	2
	+7.705348(-7)	6,55	12		-5.180810(-5)	6,64	6

TABLE I (continued)

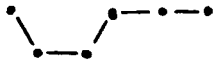
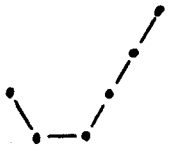
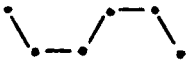
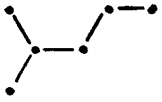
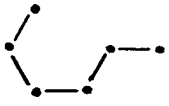
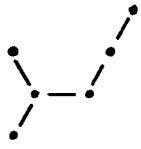
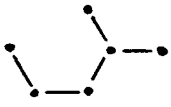
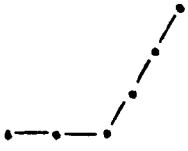
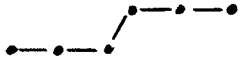
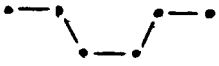
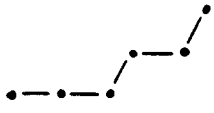
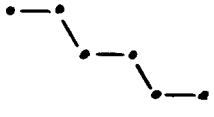
Figure	$\tilde{D}_{\ell,t}$	ℓ,t	$g_{\ell,t}$	Figure	$\tilde{D}_{\ell,t}$	ℓ,t	$g_{\ell,t}$
	-3.491259(-7)	6,65	12		-5.539132(-7)	6,74	12
	-8.660936(-8)	6,66	6		-3.511232(-7)	6,75	12
	+2.828401(-7)	6,67	12		-1.390454(-6)	6,76	6
	-8.659845(-8)	6,68	12		-3.518671(-7)	6,77	12
	-8.596544(-8)	6,69	12		+1.101327(-6)	6,78	12
	+4.487920(-7)	6,70	12		-8.652296(-7)	6,79	3
	-4.960202(-6)	6,71	12		-1.424829(-6)	6,80	6
	-7.862036(-8)	6,72	6		-3.516125(-7)	6,81	12
	+2.651832(-7)	6,73	12		-7.831841(-8)	6,82	6

Fig. 1: A section of a two dimensional triangular lattice corresponding to to the close-packed arrangement of rigid disks. The basis vectors for the lattice are given by $\underset{\sim}{a}_1$ and $\underset{\sim}{a}_2$.

Fig. 2: Successive approximations to the high-temperature constant $D_N = F_N/NkT + 2 \ln T^*$ as a function of $1/\sqrt{\ell}$, where ℓ is the order of approximation.

Fig. 3: For the triangular lattice $\Delta F = F_{Approx.} - F_{Einstein}$, the difference between the free energy for a given order of approximation and the free energy of the Einstein model is plotted as a function of $1/\sqrt{\ell}$, where ℓ is the order of approximation. Five isotherms over the temperature range $T^* = 0.4$ to 2.0 are depicted.

Fig. 4: The normal mode model for a typical six particle lattice figure (6,24 in table I.) The force constants which must be considered for nearest neighbor interactions are depicted as springs. The cartesian coordinates used in the analysis (x_i, y_i) $i = 1, \cdots, 6$ are also indicated.

Fig. 5: For a one-dimensional model the difference between the specific free energy for a given order of approximation and the exact specific free energy is plotted as a function of T^* on a logarithmic scale. The orders of approximation given are $\ell = 1$ (the Einstein model), 2,3,4,5 and 6.

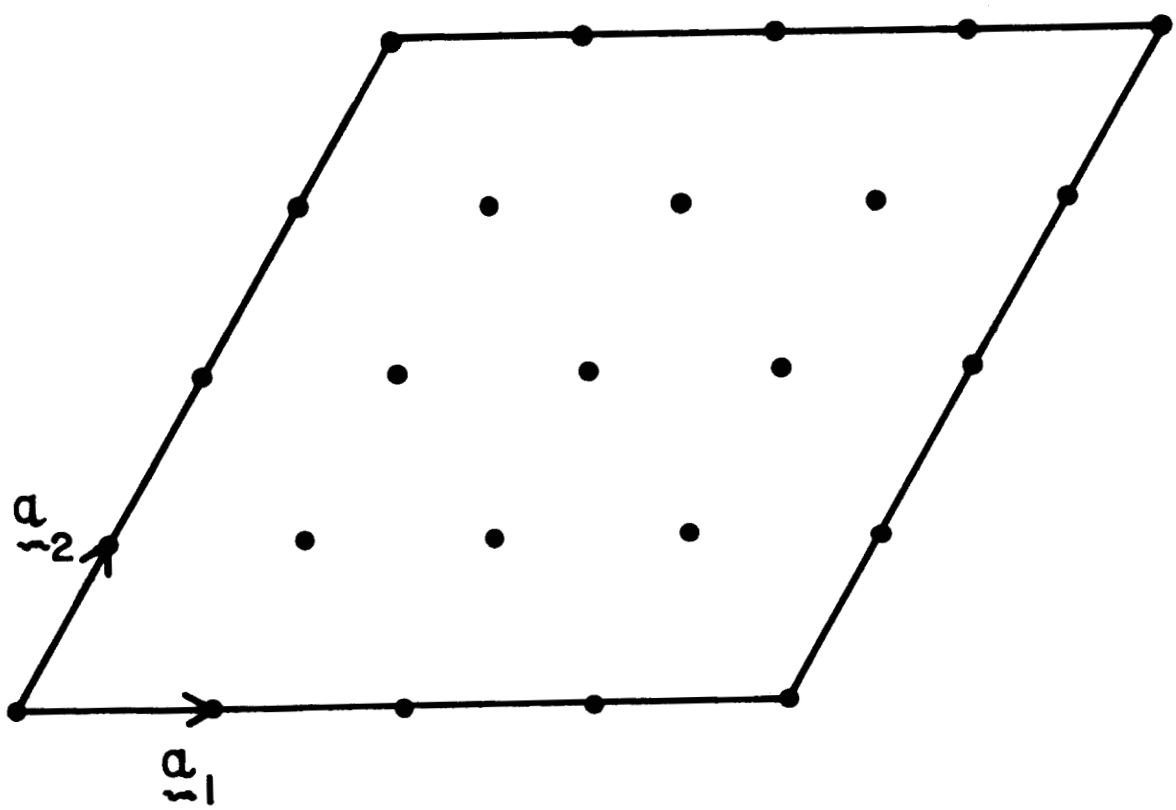


FIG. 1

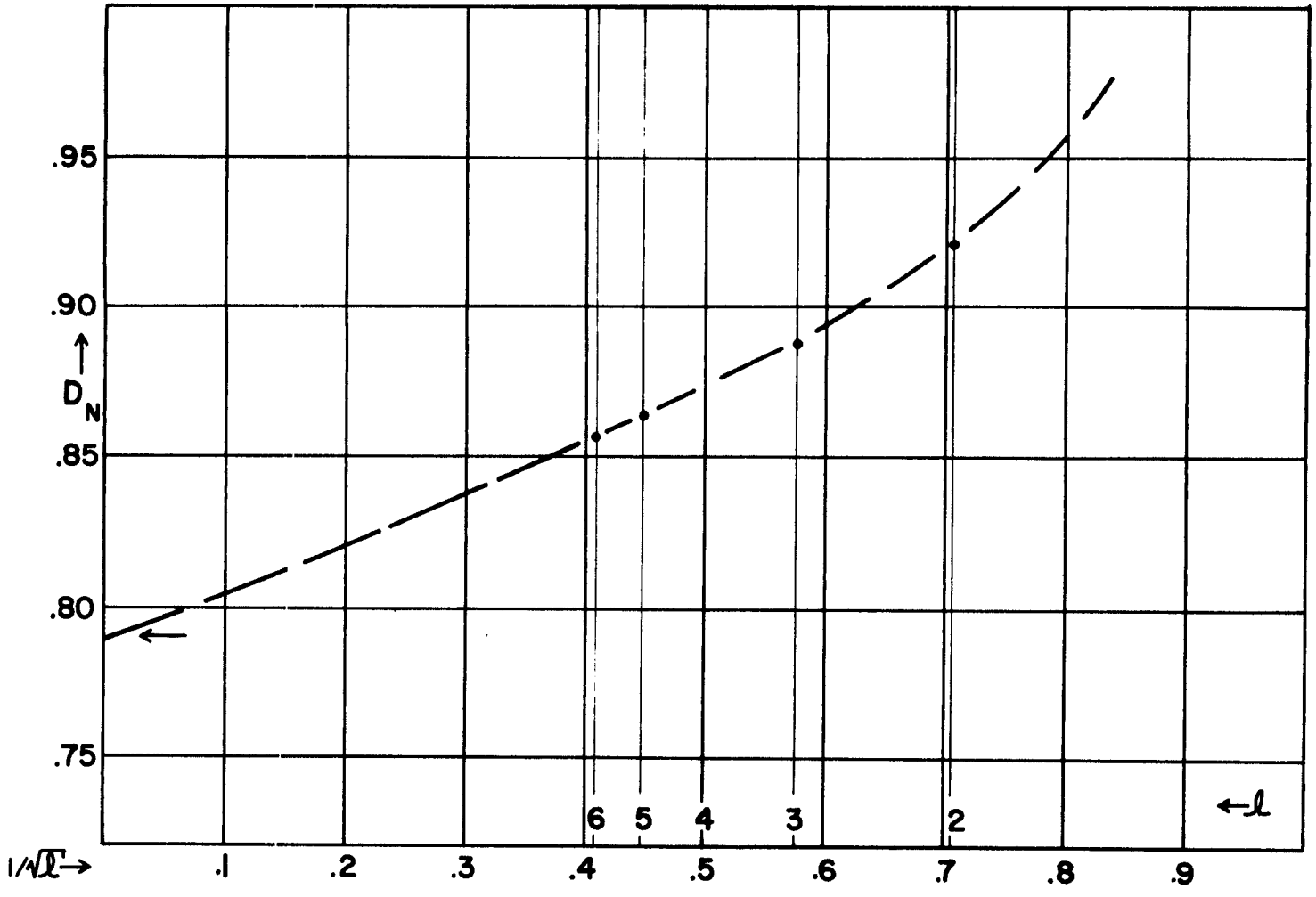


FIG. 2

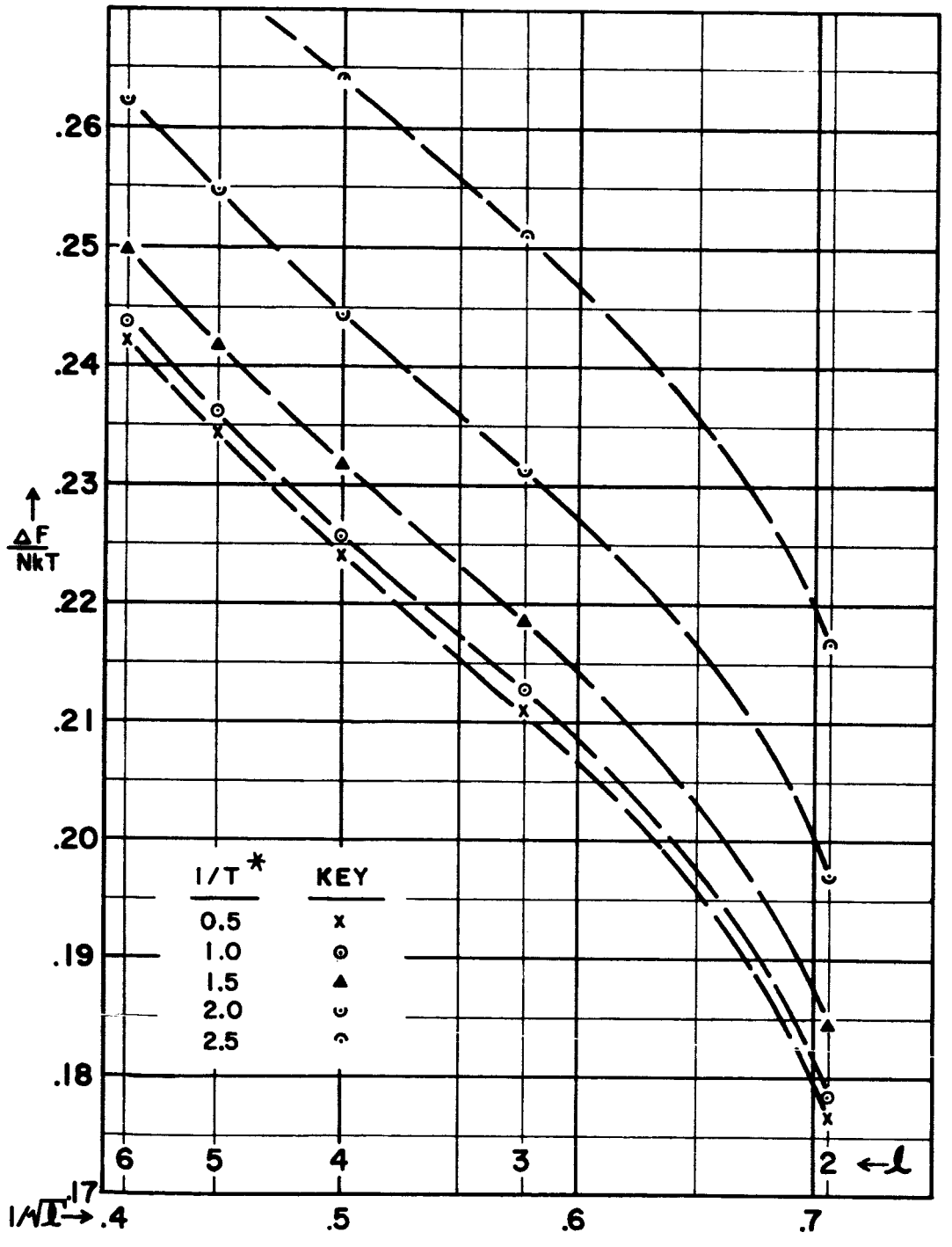

.26
.25
.24
.23
.22
.21
.20
.19
.18
.17
ΔF/NkT
1/T*
KEY
0.5
1.0
1.5
2.0
2.5
6
5
4
3
2
l
1/√T
.4
.5
.6
.7

FIG. 3

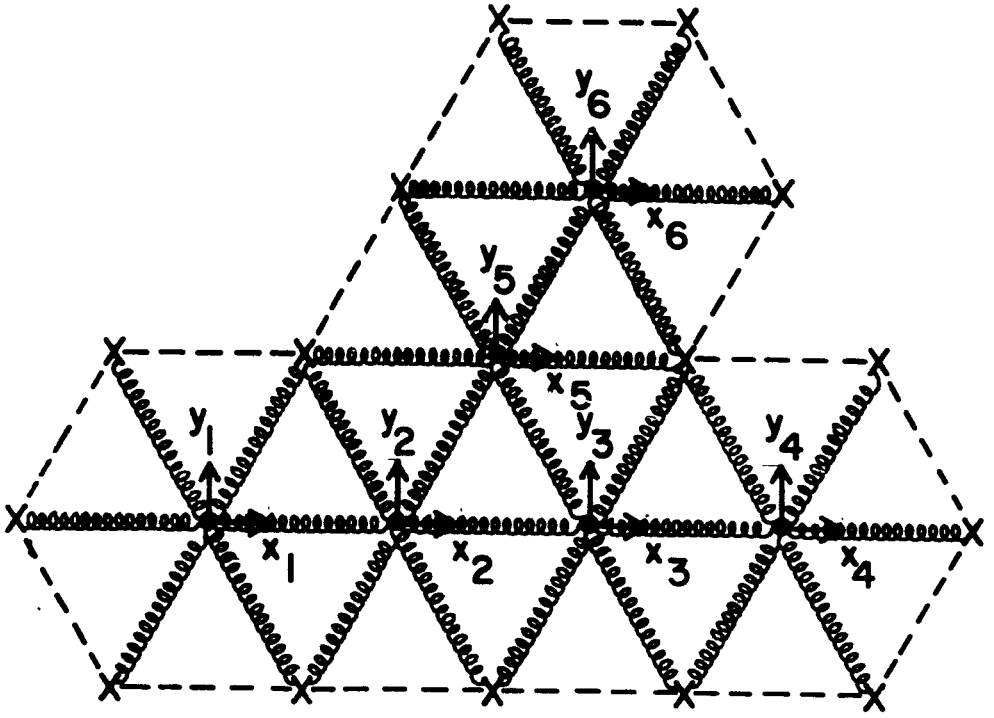


FIG. 4

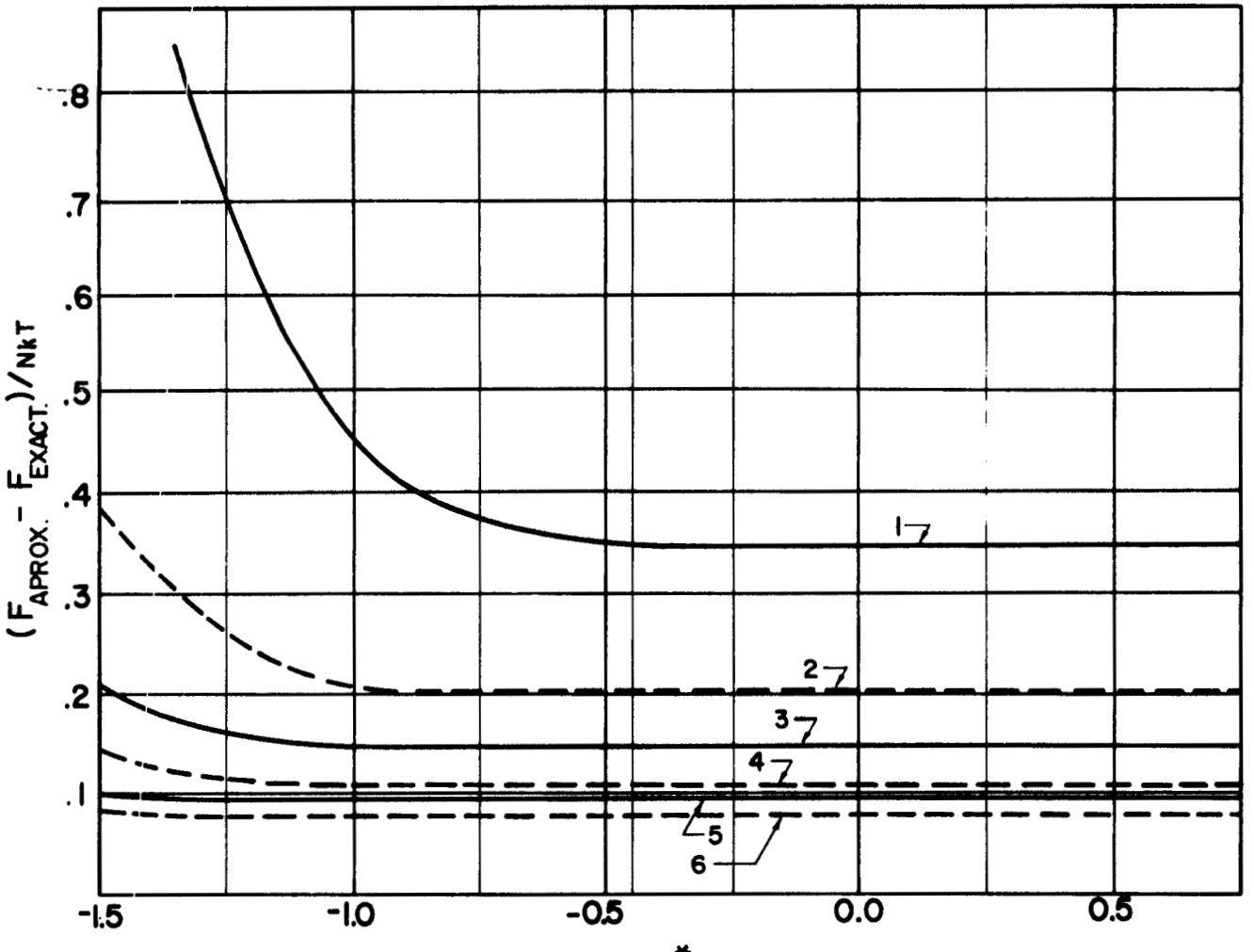


FIG. 5